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# The Use of Permutit in Water Softening

Chemical Engineering

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# THE USE OF PERMUTIT IN WATER SOFTENING

BY

JAMES FRANKLIN GARRETT

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

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COLLEGE OF SCIENCE

UNIVERSITY OF ILLINOIS

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~~1913~~

UNIVERSITY OF ILLINOIS

May 29, 1913

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

JAMES FRANKLIN GARRETT

ENTITLED THE USE OF PERMUTIT IN WATER SOFTENING.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN CHEMICAL ENGINEERING

Edward Barlow

Instructor in Charge

APPROVED: W. A. Noyes

HEAD OF DEPARTMENT OF CHEMISTRY.

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# THE USE OF PERMUTIT IN WATER SOFTENING.

Permutit* is the name chosen to designate an artificial

*Chemical Review, Felt-Harz Ind. 16, 300-2.

zeolite recently produced and patented by Dr. Robert Ganz of the Royal Prussian Geological Institute of Berlin. The name "Permutit" is derived from the Latin word "permutare", meaning to exchange.

Natural zeolites were known at an early date, but there had been no scientific investigation of their properties until quite recently.* These compounds are usually hydrated forms of

Eighth Internat'l Cong. Appl'd Chem. 25, 125.

silicates of aluminium with sodium and calcium, mixtures of double silicates of aluminium and aluminium silicates, as for example, Thomsonite, Natrolite, Analcime, Apophyllite, Desmin, Chabasite, Stilbite, etc.* They are found in nature** in cavi-

*Chem. Rev. Felt-Harz Ind. 16, 300-2.
**A System of Mineralogy, Dana, P.570.

ties and veins in basic igneous rocks and less frequently in granite, gneiss, etc.

These natural zeolites and zeolitic compounds have the property of interchanging their bases, especially the alkalies and alkaline earths for each other and for other bases. They play an important part in vegetable life through the delivery of

the natural constituents of the earth to the plants, and their restoration by means of artificial fertilizers.*

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*Woch.für Brau. 28, 78.

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All experiments in the use of the interchanging power of the natural zeolites for technical purposes have failed because of the impurity of the materials used. They contain too small an amount of the active substance, and the crystallized zeolites occur in too small quantities in nature to come into use for technical purposes. The soils which contain the zeolitic compounds are compact and heavy and therefore are little suitable for filtration purposes, because in order to do efficient work in practice the filters would have to be too large to be practicable.*

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*Chem. Rev. Felt-Harz Ind. 16, 300-2.

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Dr. Gans* has divided the aluminium zeolites into two

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*Chem. Rev. Felt-Harz Ind. 16, 300-2.

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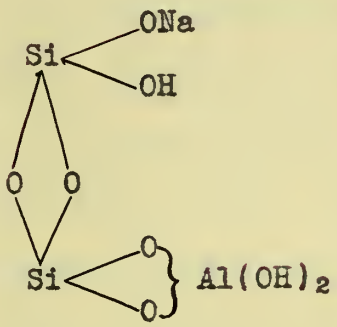
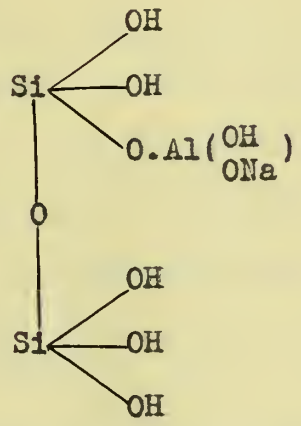
classes, viz; (1) "Double earthy silicates," --zeolites which contain the alkaline earths and alkalies mostly combined with silicic acid. The bases of these zeolites can only be substituted in a small proportion in a given time. (2) "Aluminate silicates," which are known commercially as Permutit, --zeolites which contain the alkaline earths and alkalies combined mostly with clay. The bases of these zeolites can be almost completely substituted in a very short time.

An example of the first class is analcime with the

formula: $Na_2Al_2Si_4O_{12} + 2H_2O$, which can be represented graphically as follows:




An example of the second class is Chabasite with the formula: $Na_2Al_2Si_4O_{12} + 6H_2O$, which can be represented graphically as follows:




The latter class of zeolites are of much greater importance technically than the first class because of their great power of interchanging bases, which will be explained in more detail later.

Although several investigators had experimented upon the artificial production of zeolites, Gans was the first to succeed in producing the "aluminate silicates." However Rüempler* pro-

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*Chem. Ind. 32, 197-200.

duced an artificial zeolite before Gans, but it was of the "double earthy silicate" type and was of very little technical importance because of its small interchanging power. Gans prepared his artificial zeolite by smelting together three parts of kaolin, six parts of sand, and twelve parts of soda, and washing out the excess of soda with water. The permutit, in order to be of technical importance, must be of a grainy, leafy and easily penetrable character, hence an excess of alkali must be avoided as much as possible as it tends to form a more or less slimy product. Gans* claims that a part of the soda can be re-

*Chem. Ind. 32, 197-200.

placed with potash or cheaper, with potassium feldspar or other potassium bearing rocks. The grains of the permutit are in this way made larger and more porous and thus a higher facility of reaction is obtained. The most difficult part in the manufacture of permutit* is the regulation of the point of hydration.

Eighth Internat'l Cong. Appl'd Chem. 25, 125.

If the hydration is carried too far it causes decay, and if stopped too soon, products of a feldspar nature are obtained.

Permutit contains alkali and alkaline earth bases, combined with the aluminium and silica in the molecule. These bases are easily interchangeable with each other and with other bases by treatment with the appropriate salt solutions. The facility of interchange depends upon the large size of the grains of permutit and to a more or less extent upon the amount of

bases present. The larger the amount of bases present, the greater the interchanging power of the permutit. Since one molecule of $Al_2O_3$ always combines with one molecule of $Na_2O$ (or $K_2O$), or in other words the content of clay determines the content of bases, hence Gans devoted his efforts to raising the clay content as high as possible and thus at the same time reach the maximum base content. The ideal composition of such a zeolite would approach the formula: $2SiO_2 \cdot Al_2O_3 \cdot Na_2O + 6H_2O$.

The most important characteristics of permutit are:

(1). Its property of interchanging bases,

(2). Its property of regeneration,

(3). Its insolubility in water,

(4). Its permeability, and

(5). Its length of life.

1. Its property of interchanging bases. This property is very significant, as by replacing the sodium base by other bases it is possible to make a permutit of almost any metallic combination.* Those of greatest interest, however, are the ex-

*Textile World Record, Boston, Nov. 1912. T. R. Duggan.

chagne of sodium for calcium and magnesium by which the hardness of water can be reduced to zero.

However* the application possibilities of permutit do

*Chem. Ind. 32, 197-200.

not depend upon the pure interchange as will be shown later. The following examples will show the manner of the change of bases in different processes.

(a) "Separation of undesirable bases from solution by a simple interchange whereby the resulting salts are water soluble:"

$2SiO_2 \cdot Al_2O_3 \cdot Na_2O + CaCl_2 = 2SiO_2 \cdot Al_2O_3 \cdot CaO + 2NaCl$

$2SiO_2 \cdot Al_2O_3 + 2NaCl = 2SiO_2 \cdot Al_2O_3 \cdot Na_2O + CaCl_2.$

(b) "Separation of undesirable salts from solution whereby not only the bases but also the acids are separated and the resulting salts are insoluble in water:"

Ex. 1: $2SiO_2 \cdot Al_2O_3 \cdot CaO + Na_2CO_3 = 2SiO_2 \cdot Al_2O_3 \cdot Na_2O + CaCO_3.$

Ex. 2: $2SiO_2 \cdot Al_2O_3 \cdot BaO + CaSO_4 = 2SiO_2 \cdot Al_2O_3 \cdot CaO + BaSO_4.$

Ex. 3: $2SiO_2\ Al_2O_3\ Ag_2O + 2NH_4Cl = 2SiO_2\ Al_2O_3\ (NH_4)_2O + AgCl.$

(c) "Application of contact surfaces through single and double interchanges to the precipitation of bases from solution:"

Ex. 1: $2SiO_2 \cdot Al_2O_3 \cdot Na_2O + SnCl_2 = 2SiO_2 \cdot Al_2O_3 \cdot SnO + 2NaCl.$

Ex.2a: $2SiO_2 \cdot Al_2O_3 \cdot CaO + MnCl_2 = 2SiO_2 \cdot Al_2O_3 \cdot MnO + CaCl_2.$

Ex.2b: $2SiO_2 \cdot Al_2O_3 \cdot MnO + CaMn_2O_8 = 2SiO_2 \cdot Al_2O_3 \cdot CaO + MnO \cdot Mn_2O_7.$

Ex.2c: $2SiO_2 \cdot Al_2O_3 \cdot CaO + MnO \cdot Mn_2O_7 + 2MnH_2(CO_3)_2 =$

$2SiO_2\ Al_2O_3\ CaO + 5MnO_2 + 2H_2O + 2CO_2.$

(d) "Separation of free alkali from solution:"

The zeolites have the property of adding free alkali from dilute solutions and of giving them up again upon contact with strongly acid solutions.

The type of reaction as given under process (a) is perhaps of the greatest technical importance because all the calcium and magnesium salts of a hard water can in this way be converted to calcium and magnesium permutit, by replacing the sodium which combines with the acids in the water. Thus the hardness is completely removed.

Type (c) is also important, as by means of Ex. 1, gold

may be precipitated from dilute solutions. A large surface of active SnO is obtained which precipitates the gold, not through a direct interchange, but through the contact action of the SnO.

Exs. 2a and 2b of process (c) show a method of demanganizing water. The manganese compound, $MnO \cdot Mn_2O_7$, is solidly attached in and around the permutit grains, in such a manner that a large surface is exposed, which oxidizes the manganese and iron in a water and thus precipitates them from solution.

2. Its property of regeneration. When one of the above processes is carried out for any great length of time, the base content of the permutit eventually becomes exhausted, hence it is necessary to regenerate it. The regeneration can be accomplished by passing through it a solution containing the original base. For example, in the case of sodium permutit, the sodium is replaced by the calcium and magnesium of hard water and when it is exhausted the permutit can be regenerated by passing through it a 10 per cent solution of common salt (NaCl), the interchange taking place in the opposite direction. In like manner manganese permutit may be regenerated by passing through it a solution of $CaMn_2O_8$.

3. Another important property of permutit is that all of its salts, also those of the alkalies, are insoluble in water.

4. The permeability of permutit is also important, because its high interchanging facility depends on the fact that the water penetrates the interior of the grains and hence the whole of the substance is brought into action and not merely the external surfaces of the grains.

5. Its length of life. It is claimed* that permutit

*Textile World Record, Boston, Nov. 1912. T. R. Duggan.

can be regenerated an unlimited number of times without loss, hence it is never necessary to renew it. However, I have found that there is a small loss of permutit in washing the filter, but this loss is purely mechanical and by exercising a little care in flushing can be reduced to a minimum.

The industrial uses claimed for permutit are many and varied. Harm and Ruempler were the first to point out a technical use* for the interchanging power of zeolites. This was in

*Chem. Ind. 32, 197-200.

the sugar industry. They tried exchanging the potassium salts of the sugar sap for calcium and they showed by experiments that the calcium salts hinder the crystallization of sugar much less than do the corresponding potassium salts. The process is a pure interchange and consists simply of filtering the sugar sap through a calcium zeolite and regenerating the latter by means of $CaCl_2$ solution. In this way the potassium salts may also be recovered, which are valuable for fertilizer purposes. However the interchanging power of Ruempler's zeolite was too low to make it of commercial importance, but the high interchanging power of permutit eliminates this objection and it bids fair to become an important factor in the sugar manufacture of the future because by its use, the sap is clarified, the sugar output is increased, and the potassium salts are recovered by one operation.

Another possible technical application of permutit, which I have pointed out before, is the recovery of gold from dilute solutions.

The manufacture of the salts of bases by double exchange has a wide range of possibilities in this process. For example, if sodium permutit is washed with a solution of $NH_4Cl$* an ammon-

*Eighth International Cong. Appl'd Chem. 25, 125.

ium permutit is produced.

$$Per\text{-}Na_2 + 2NH_4Cl = Per\text{-}(NH_4)_2 + 2NaCl.$$

By passing waste waters containing potassium salts through this permutit, it is changed to potassium permutit as follows:

$$Per\text{-}(NH_4)_2 + 2KCl = Per\text{-}K_2 + 2NH_4Cl.$$

By regenerating this filter with $NH_4Cl$ the potassium may be recovered:

$$Per\text{-}K_2 + 2NH_4Cl = Per\text{-}(NH_4)_2 + 2KCl.$$

By far the greatest possibilities for commercial application of permutit, however, lies in its use for the purification and softening of water.

The process differs from most water softening processes in that an excess of insoluble reagent is used instead of a small amount of a soluble one.

Permutit is used, in the purification of water, in two forms, namely: (1) manganese permutit for the removal of iron, manganese, organic matter, and bacteria, and (2) sodium permutit for the removal of calcium and magnesium.

The manganese-permutit is prepared* by passing a solu-

*Chem. Ztg. 35, 1393-1420.

tion of $MnCl_2$ through sodium permutit and then washing with calcium or potassium permanganate:

$$2SiO_2 \cdot Al_2O_3 \cdot Na_2O + MnCl_2 = 2SiO_2 \cdot Al_2O_3 \cdot MnO + 2NaCl.$$

$$2SiO_2 \cdot Al_2O_3 \cdot MnO + CaMn_2O_8 = 2SiO_2 \cdot Al_2O_3 \cdot CaO + MnO \cdot Mn_2O_7.$$

The higher oxides of manganese which are formed cling mechanically to the granules of permutit, thus exposing a very large, highly oxidized surface.

This process may be used* to remove iron and manganese

*Chem. Ind. 32, 197-200.

from water even though they are present in very small quantities. The iron and manganese, upon coming in contact with the oxides of manganese, are oxidized and precipitated upon the filter. The precipitated manganese is attached solidly to the grains of permutit, thus adding to the manganese content of the filter, while the iron forms a loose precipitate which can be washed out of the filter by back flushing. The organic matter contained in the water can be removed in the same manner. The process may also be used for sterilizing water. By treating a water with $CaMn_2O_8$ it is made sterile, then by filtering over the manganese permutit the sterilizing material is removed. Nothing is lost in the latter operation if carried out in connection with the iron and manganese removal process because the manganese permutit can be regenerated by passing through it, a solution of $CaMn_2O_8$ .

The use of sodium permutit for softening water is, per-

haps, of greatest commercial importance because of the large number of industries that require water free from calcium and magnesium. The sodium-permutit filter will reduce the hardness of almost any water to zero and at a very low cost. Hence the advantages of permutit-treated waters for boiler purposes, dyeing, bleaching, laundry work, etc., are undoubtedly very great.

The essential difference* in the action of the sodium-

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*National Laundry Journal, Chicago, Mar. 15, 1912.

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permutit and the manganese-permutit is, that in softening water by sodium-permutit, the substances eliminated from the water actually enter into combination with the permutit and consequently there is no precipitation and no clogging up of the filter, but in the manganese-permutit the oxidizable substances in the water are actually precipitated and tend to clog up the filter.

When a hard water (i.e. water containing salts of calcium and magnesium) is filtered through a bed of sodium permutit, the sodium in the permutit is replaced by the calcium and magnesium of the water, forming a calcium-magnesium-permutit, while the sodium unites with the acid radicles in the water, according to the following reactions:

$$2SiO_2 \cdot Al_2O_3 \cdot Na_2O + CaH_2(CO_3)_2 = 2SiO_2 \cdot Al_2O_3 \cdot CaO + 2NaHCO_3.$$

$$2SiO_2 \cdot Al_2O_3 \cdot Na_2O + MgH_2(CO_3)_2 = 2SiO_2 \cdot Al_2O_3 \cdot MgO + 2NaHCO_3.$$

The reactions are similar for all other salts of calcium and magnesium. The regeneration reaction is as follows:

$$2SiO_2 \cdot Al_2O_3 \cdot (Ca,Mg)O + NaCl = 2SiO_2 \cdot Al_2O_3 \cdot Na_2O + (Ca,Mg)Cl_2.$$

## EXPERIMENTAL PART.

A number of experiments have been made in the chemical laboratory of the University of Illinois to determine the effect produced by filtering hard water through a bed of sodium permutit.

The filter used in the investigations consists of a steel shell, twelve inches in diameter and sixty inches in height. The outlet is covered by an inverted disk slightly raised at the edge to permit the water to flow under it. On the disk is a layer of gravel about eight inches in depth. Eighty pounds of permutit are placed on top of the gravel. Supported on a perforated steel plate about twelve inches above the top of the layer of permutit, is another layer of gravel, about three inches in thickness. A single pipe on the outside of the filter is equipped with valves and connections so that it can be used simultaneously for the inlet and outlet for water. By regulating the valves this pipe can also be used to backflush the filter, and to drain out the salt solution, used in the regeneration. A float valve fitted on the inlet pipe regulates the flow. An overflow pipe is provided for use during the back flushing of the filter. A porcelain-lined iron tank, elevated above the filter, with a capacity of eight gallons is used for dissolving the salt and feeding the solution into the filter while regenerating.

The filter is designed to soften 33 gallons per hour for 12 hours. However, I have found that the filter will run at the above rate for about 16 hours, with water containing

280 parts per million carbonate hardness, before it is necessary to regenerate.

The regeneration of the filter is accomplished by dissolving eight pounds of common salt in eight gallons of water, running this solution into the filter and letting it stand for about six hours, (usually over night). Then the salt solution is drained out and water forced upward (back-flushing) through the filter for a short time to wash out the dirt, etc., which may have collected on the filter. Then the filter is started. It requires from ten to fifteen minutes to wash out the last traces of salt after which the water is ready for use.

The University tap water, which contains no sulfates has been used for a number of runs with this filter. A well water containing a large quantity of sulfates has been used for one run. Samples were taken at intervals during these runs and the following tests were made:

(1) Non-carbonate hardness,

(2) Magnesium (as $CaCO_3$),

(3) Alkalinity,

(4) Calcium as ($CaCO_3$),

(5) Sodium Carbonate,

(6) Chlorine,

(7) Iron.

The methods of making these tests are as follows:

(1)."Determination of Non-carbonate hardness.--200 cc. of the water are placed into a 500 cc. Erlenmeyer falsk, and boiled for 15 minutes to expel the $CO_2$. Then 25 cc. N/20 soda

reagent,--a mixture of equal parts NaOH and $Na_2CO_3$,--are added, boiled 10 minutes and filtered into a 200 cc. flask. In an aliquot portion the excess of alkali is titrated with N/50 $H_2SO_4$ using methyl orange as an indicator. A blank determination is also made using distilled water.

"The difference between the number of cc. used for the blank and the number of cc. used for the water is the non-carbonate hardness (N. C. H.) in terms of $CaCO_3$.

"If the water contains $Na_2CO_3$ the number of cc. used for the blank determination will be less than that used for the water.

(2). "Determination of Magnesium--Rapid Method. 100 cc. of the water (the portion in which the alkalinity was determined may be used) is neutralized carefully with N/50 $H_2SO_4$, to methyl orange in a 200 cc. graduated flask and heated on a hot plate to expel the $CO_2$.

"25 or 50 cc. of saturated lime water are added. This is allowed to stand on a water bath for about 15 minutes, to allow the precipitate to settle completely. It is then made up to about 5 cc. above the mark to allow for contraction, shaken thoroughly and allowed to cool.

"The excess of lime water is determined by titrating with N/50 $H_2SO_4$ and methyl orange indicator, an aliquot portion of the supernatant liquid or filtrate being used.

"At the same time a blank of distilled water is treated in the same way. The difference between the titration of the blank and the water represents the amount of magnesium present

in terms of $CaCO_3$."

(3). Determination of Alkalinity. The alkalinity was determined by simply titrating 100 cc. of the water against N/50 $H_2SO_4$. Methyl orange was used as an indicator.

(4). The calcium was determined by calculation as follows:

Alk - (Mg as $CaCO_3$ + N.C.H.) = $CaCO_3$.

(5). The sodium carbonate was also determined by calculation:

Negative, N.C.H. X 1.06 = $Na_2CO_3$.

(6). The chlorine was determined by titrating against silver nitrate solution, using $K_2CrO_4$ as an indicator.

(7). The iron was determined by the colorimetric method.

Although these tests do not give as much information as does the method of making complete mineral analyses, yet they can be rapidly carried out and serve very well to show the comparisons between the raw and treated waters and the efficiency of the permutit.

The following are complete records of the runs made with the filter.

Run No. I.

January 30. Filter started at 3:00 p.m.

Sample #1. Raw tap water.

Sample #2. Taken 3:15 p.m. Rate 32.7 gal. per hour.

Sample #3. " 3:30 " " 48.5 " " "

Sample #4. " 3:55 " " 26.3 " " "

Filter stopped at 4:00 p.m.

February 6. Filter started 8:15 a.m.

Sample #5. Taken 8:20 a.m. Rate 35 gal. per hour.
Water pinkish in color. Had been standing in filter several days.

Sample #6. Taken 11:30 a.m. Rate 35 gal. per hour.

Sample #7. " 3:45 p.m. " 33.5 " " "

Filter stopped at 3:45 p.m.

February 11. Filter started 8:00 a.m.

Sample #8. Taken 9:00 a.m. Rate 31.6 gal. per hour.

Sample #9. " 11:00 " " 28.7 " " "

Sample #10. " 1:00 p.m. " 27.8 " " "

Sample #11. " 3:00 " " 26.3 " " "

Filter stopped at 3:25 p.m.

Filter run a total of 16.6 hours without regeneration.

RESULTS OF ANALYSES OF SAMPLES -- RUN NO. I.

| No. | Kind | N.C.H. | Alk. | Mg as $CaCO_3$ | $MgCO_3$ | $CaCO_3$ | $Na_2CO_3$ | Gal. per Hour. |
|---|---|---|---|---|---|---|---|---|
| 1 | Raw | - 80 | 358 | 148 | 125 | 130 | 85 | ------ |
| 2 | Treated | -550 | 553 | 00 | 00 | 3 | 583 | 32.7 |
| 3 | " | -460 | 472 | 00 | 00 | 12 | 488 | 48.5 |
| 4 | " | -456 | 477 | 00 | 00 | 21 | 483 | 26.3 |
| 5 | " | -808 | 810 | 00 | 00 | 2 | 856 | 35.0 |
| 6 | " | -394 | 422 | 00 | 00 | 28 | 418 | 35.0 |
| 7 | " | -388 | 399 | 00 | 00 | 11 | 411 | 33.5 |
| 8 | " | -408 | 416 | 00 | 00 | 8 | 432 | 31.6 |
| 9 | " | -374 | 387 | 00 | 00 | 13 | 396 | 28.7 |
| 10 | " | -394 | 407 | 00 | 00 | 13 | 418 | 27.8 |
| 11 | " | -376 | 389 | 8 | 6.8 | 21 | 399 | 26.3 |

REMARKS.

The above results show a large increase in the alkalinity of the water after treatment with permutit. The greater part of this is doubtless due to absorption by the water of sodium carbonate from the permutit, because an excess of sodium carbonate is used in the manufacture of permutit. This explanation is further borne out by sample #5 which was taken from water that had stood in the filter for several days, and which showed an abnormal alkalinity.

However the alkalinity of the treated water gradually becomes lower with use of the filter as will be shown by the results which follow.

But the alkalinity of the treated water continues to be somewhat higher than that of the untreated water even with long use of the filter. It is probably due to the $CO_2$ in the water which decomposes the permutit and forms $Na_2CO_3$ according to the following reaction:

$$2SiO_2 - Al_2O_3 \cdot Na_2O + CO_2 = Na_2CO_3 + 2SiO_2 \cdot Al_2O_3.$$

The $Na_2CO_3$ in turn reacts with the calcium-permutit and forms calcium carbonate, as follows:

$$2SiO_2 \cdot Al_2O_3 \cdot CaO + Na_2CO_3 = CaCO_3 + 2SiO_2 \cdot Al_2O_3 \cdot Na_2O.$$

This explanation also accounts for the fact that the treated water contains a small amount of $CaCO_3$.

It is probable that only part of the $Na_2CO_3$ is changed to $CaCO_3$, the remainder being converted to $NaHCO_3$, because the concentration of the sodium would have to be greater than that of the calcium or the reaction would not go in that direction. How-

ever, the $CO_2$ can be very easily removed from the water by passing it through a bed of limestone or other similar material before admitting it to the filter.

Run, No. 2.

February 13. Regeneration of filter. Dissolved 8 lbs. of salt in 8 gallons of water. Let water run out of filter down to the level of the operating faucet. Then started salt solution flowing into the filter. Opened operating faucet, slightly, allowing about 2 gallons per hour of water to flow out. Thus all of the water was drawn off in about 6 hours and only the salt solution remained.

February 15. Salt solution was drawn off, and the filter flushed by reversing the flow of water for about 10 minutes. Note:-- Care must be taken in reversing the flow, else the water will force the permutit and gravel upwards. The float valve at the top should be left open. This will automatically regulate the pressure of the water from below.

Filter started at 2:00 p.m.

Sample #12. Taken 2:00 p.m. Rate 39.4 gal. per hour.
Tasted salty.

Sample #13. Raw water.

Sample #14. Taken 2:30 p.m. Rate 31.5 gal. per hour.
Tasted salty.

Filter stopped 3:00 p.m.

February 18. Filter started 9:00 a.m.

Sample #15. Taken 9:30 a.m. Rate 32.6 gal. per hour.

Sample #16. " 11:30 a.m. " 43.5 " " "

Sample #17. " 1:30 p.m. " 35.1 " " "

Sample #18. Taken 4:00 p.m. Rate 29.3 gal. per hour.

Filter stopped at 5:00 p.m.

February 20. Filter started at 8:00 a.m.

Sample #19. Raw water.

Sample #20. Taken 10:00 a.m. Rate 29.3 gal. per hour.

Sample #21. " 11:00 a.m. " 27.8 " " "

Filter stopped at 11:00 a.m.

Filter run 12 hours.

Water appeared to be hard with ordinary soap. However an analysis of last sample showed that the filter was not exhausted.

RESULTS OF ANALYSES OF SAMPLES -- RUN NO. II.

| No. | Kind | N.C.H. | Alk. | Mg as $CaCO_3$ | $MgCO_3$ | $CaCO_3$ | $Na_2CO_3$ | Cl. | Gal.per Hour |
|---|---|---|---|---|---|---|---|---|---|
| 12 | Treated | +172 | 329 | 332 | 280 | 169 | ---- | 9496. | 39.4 |
| 13 | Raw | - 68 | 351 | 116 | 98 | 167 | 72 | 1. | ---- |
| 14 | Treated | -302 | 400 | 140 | 118 | --- | 320 | 6996. | 31.5 |
| 15 | " | -384 | 394 | 00 | 00 | 10 | 407 | 18. | 32.6 |
| 16 | " | -370 | 387 | 00 | 00 | 17 | 392 | 2. | 43.5 |
| 17 | " | -352 | 370 | 00 | 00 | 18 | 373 | 1. | 35.1 |
| 18 | " | -376 | 386 | 00 | 00 | 10 | 399 | 1. | 29.3 |
| 19 | Raw | - 98 | 336 | 100 | 84 | 138 | 104 | 1. | ---- |
| 20 | Treated | -356 | 361 | 00 | 00 | 5 | 377 | 1. | 29.3 |
| 21 | " | -384 | 382 | 00 | 00 | 0 | 407 | 1. | 27.8 |

REMARKS.

The first three samples of treated water, in this case, were taken before the salt solution was completely washed out of

the filter, as is shown by the high chlorine content, and also by the magnesium content which is much higher than in the raw water. The other samples show that all of the magnesium and most of the calcium is removed by treatment with permutit.

Run, No. 3.

February 20. 1:00 p.m. Filter was regenerated in same manner as in run No. 2.

February 25. 8:00 a.m. Salt solution was drained out of the filter and the filter back-flushed for about 10 minutes. The water tasted salty so the filter was started at 9:30 at a rate of 43 gallons per hour and at 9:40 the water ceased to taste salty.

Sample #22. Taken 9:40 a.m. Rate 38 gal. per hour.
Sample #23. " 11:00 a.m. " 27 " " "
Sample #24. " 12:00 M. " 37 " " "
Sample #25. " 1:00 p.m. " 25 " " "

The filter seemed to be packed and the water would not run through it with sufficient rapidity. A reversed flow with heavy pressure for a short time loosened the filter bed and it filtered as rapidly as desired.

Sample #26. Taken 2:30.p.m. Rate 45 gal. per hour.
Sample #27. " 4:30 p.m. " 38 gal. " "

Filter stopped 4:45 p.m.

## RESULTS OF ANALYSES OF SAMPLES -- RUN NO. III.

| No. | Kind | N.C.H. | Alk. | Mg as $CaCO_3$ | $MgCO_3$ | $CaCO_3$ | $Na_2CO_3$ | Gal. per Hour. |
|---|---|---|---|---|---|---|---|---|
| 22 | Treated | -394 | 410 | 000 | 000 | 12 | 418 | 38 |
| 23 | " | -378 | 377 | 000 | 000 | 0 | 401 | 27 |
| 24 | " | -374 | 387 | 000 | 000 | 13 | 396 | 37 |
| 25 | " | -384 | 380 | 000 | 000 | 0 | 407 | 25 |
| 26 | " | -350 | 357 | 24 | 20 | 31 | 371 | 45 |
| 27 | " | -368 | 368 | 000 | 000 | 0 | 390 | 33 |
| 28 | " | -356 | 360 | 000 | 000 | 4 | 377 | 33 |
| 29 | " | -324 | 344 | 000 | 000 | 20 | 343 | 37. |

February 26. Filter started 1:00 p.m. Stopped 4:00 p.m.

No samples taken. Rate 32 gal. per hour.

February 27. Filter started 8:00 a.m. Rate 38 gal. per hr.

Total hardness (T.H.) was determined in the following samples by titrating 50 cc. of water against standard alcoholic soap solution:

Sample #I. Taken 9:30 a.m. Total hardness = 0

Sample #II. Taken 12:00 M. " " = 0

Sample #III. Taken 1:00 p.m. " " = 0

Sample #IV. Taken 3:30 p.m. " " = 6 p.p.m. $CaCO_3$

Sample #28. Taken 3:30 p.m. Rate 33 gal. per hour.

Filter stopped 3:30 p.m. Run 17-1/2 hours.

February 28. Filter started 1:00 p.m. Rate 41 gal. per hr.

Sample #V. Taken 2:00 p.m. Total hardness = 6 p.p.m.

Sample #29. Taken 4:00 p.m. Rate 37 gal.per hour.

Filter left running over night.

March 1. Sample #VI. Taken 9:30 a.m. Rate 10 gal. per hr.

Total hardness = 105 p.p.m. $CaCO_3$.

Filter having run 38 hours without regeneration.

Regenerated the filter.

REMARKS.

Sample #26 shows that the filter will not completely soften the water if it is run through with too great speed. This is an important point in the design of permutit filters. It shows that there is a limit to the rate of flow through the bed of permutit. In order to get efficient results the water must be given time to penetrate the grains and bring all the material into use. Time must also be given for the reactions to take place.

Run, No. 4.

March 4. Drained out the salt solution and reversed the flow for 15 minutes. Started filter at 10:15 a.m.

Sample #30. Taken 10:30 a.m. Rate 38 gal. per hour.

Tasted salty. Salt taste disappeared 10:45 a.m.

Total hardness of #30 = 180 p.p.m. $CaCO_3$.

Sample #31. Taken 1:00 p.m. Rate 38 gal. per hour.

Total hardness of #31 = 7 p.p.m. $CaCO_3$

Sample #32. Taken 4:00 p.m. Rate 38 gal. per hour.

Filter stopped 4:00 p.m.

March 6. Filter started 8:00 a.m.

Rate 38 gal. per hour.

Sample taken at 9:00 a.m. T. H. = 0. Rate 38 gal. per hour.
" " " 10:00 " " " " " " 38 " " "
" " " 11:00 " " " " " " 38 " " "
" " " 12:00 M. " " " " " 38 " " "
" " " 1:00 p.m. " " " " " 32 " " "
" " " 2:00 " " " " " 37 " " "
" " " 3:00 " " " " " 39 " " "
" " " 4:00 " " " " " 32 " " "
" " " 5:30 " " " 25 p.p.m. " 41 " " "

Sample #33. Taken 5:30 p.m. Rate 41 gal. per hour.

Filter stopped at 5:30 p.m.

Run 15 hours without regeneration.

Filter regenerated, for exhibition at the meeting of the Illinois Water Supply Association.

RESULTS OF ANALYSES OF SAMPLES -- RUN NO. IV.

| No. | Kind | N.C.H. | Alk. | Mg as $CaCO_3$ | $MgCO_3$ | $CaCO_3$ | $Na_2CO_3$ | Iron | Gal. per Hour. |
|---|---|---|---|---|---|---|---|---|---|
| 30. | Treated | +330 | 288 | 320 | 269 | 288 | --- | .1 | 38 |
| 31 | " | -356 | 373 | 000 | 000 | 16 | 378 | 000 | 38 |
| 32 | " | -354 | 369 | 000 | 000 | 15 | 375 | trace | 35 |
| 33 | " | -326 | 362 | 000 | 000 | 36 | 346 | trace | 41 |

Run No.5

March 17. Filter regenerated.

March 18. Salt solution drained out and the filter flushed and started at 10:00 a.m.

Sample #34. Taken 11:00 a.m. Rate 31 gal. per hour.

Sample #35. " 11:45 a.m. " 34 " " "

Sample #36. Taken 1:00 p.m. Rate 39 gal. per hour.

Sample #37. Raw water.

Sample #38. Taken 2:00 p.m. Rate 38 gal. per hour.

Sample #39. " 3:00 p.m. " 31.5 gal. per hour.

Filter stopped at 4:00 p.m.

March 20. Filter started 8:00 a.m.

Filter stopped at 10:00 a.m.

March 27. Filter started 9:00 a.m.

Filter stopped at 1:00 p.m.

April 3. Filter started 9:30 a.m.

Sample taken at 10:30 a.m. T. H. = 0 Rate 36 gal. per hour.

" " " 11:30 " " " " " 41 " " "

" " " 12:30 p.m. " " 6 p.p.m " 34 " " "

" " " 1:30 " " " 18 " " 36 " " "

Filter exhausted about 12:30 after running 15 hours without regeneration. Filter regenerated.

RESULTS OF ANALYSES OF SAMPLES -- RUN NO. V.

| No. | Kind | N.C.H. | Alk. | Mg as $CaCO_3$ | $MgCO_3$ | $CaCO_3$ | $Na_2CO_3$ | Iron | Gal.per Hour. |
|---|---|---|---|---|---|---|---|---|---|
| 34 | Treated | -364 | 357 | 000 | 000 | 0 | 386 | 000 | 31 |
| 35 | " | -364 | 361 | 000 | 000 | 0 | 386 | 000 | 34 |
| 36 | " | -362 | 354 | 000 | 000 | 0 | 384 | trace | 39 |
| 37 | Raw | - 74 | 327 | 96 | 81 | 157 | 78.5 | 1.3 | --- |
| 38 | Treated | -364 | 359 | 000 | 000 | 0 | 386 | 000 | 38 |
| 39 | " | -364 | 359 | 000 | 000 | 0 | 386 | 000 | 31.5 |

REMARKS.

The above results show that the iron is completely removed from water by passing it through a sodium permutit filter.

Run No. 6.

April 21. Filter drained and flushed.

Filter started 1:00 p.m.

Salt was all washed out at 1:45 p.m.

Sample taken at 1:45 p.m. T. H. = 0 Rate 34 gal. per hour.
" " " 2:45 " " " " " 34 " " "
" " " 3:45 " " " " " 32 " " "
" " " 5:00 " " " " " 32 " " "

Filter stopped 5:00 p.m.

April 22. Filter started at 9:00 a.m. Rate 34 gal. per hr.

Sample taken at 10:00 a.m. T. H. = 0 Rate 34 gal. per hour.
" " " 11:00 " " " " " 33 " " "

Took samples for mineral analysis.

Sample taken at 12:00 M. T. H. = 0 Rate 34 gal. per hour
" " " 1:00 p.m. " " " " 34 " " "
" " " 2:00 " " " " " 34 " " "
" " " 3:00 " " " " " 32 " " "
" " " 3:30 " " " " " 34 " " "

Filter stopped at 3:30 p.m.

April 23. Filter started 1:00 p.m. Rate 34 gal. per hr.

Sample taken at 2:00 p.m. T. H. = 0 Rate 34 gal. per hour
" " " 3:00 " " " " " 32 " " "

Filter stopped at 3:00 p.m.

April 24. Filter started 9:00 a.m. Rate 34 gal. per hr.

Sample taken at 10:00 a.m. T. H. = 0 Rate 34 gal. per hour

" " " 11:00 " " " " " 32 " " "

" " " 12:00 M " = 12 p.p.m. " 34 " " "

" " " 1:00 p.m. " = 25 " " 34 " " "

Filter exhausted about 12:00 after running 15 hours.

The above results show that, without removing the $CO_2$, the permutit will soften water to a point where it cannot be detected by titrating against a standard soap solution. This is sufficient for most technical purposes.

## MINERAL ANALYSES OF RAW AND TREATED WATER.

Note--The sample of the raw water was collected about two weeks before the sample of treated water, hence the analyses show variations not due to the permutit.

| (Results expressed in parts per million) | | Raw | Treated |
|---|---|---|---|
| Residue on evaporation | | 386. | 449. |
| Silica | $SiO_2$ | 20.5 | 21. |
| Sulfates | $SO_4$ | 1.5 | 0.4 |
| Iron | Fe | 1.3 | .0 |
| Aluminium Oxide | $Al_2O_3$ | .9 | 2.2 |
| Calcium | Ca | 70.2 | 2.5 |
| Magnesium | Mg | 32.2 | .37 |
| Sodium | Na | 27.6 | 156.2 |
| Potassium | K | 4.0 | 24.2 |
| Hypothetical Combinations | | | |
| Potassium Sulfate | $K_2SO_4$ | 2.7 | .7 |
| Potassium Carbonate | $K_2CO_3$ | 6.7 | 42.4 |

| | | Raw | Treated |
|---|---|---|---|
| Sodium Carbonate | $Na_2CO_3$ | 63.4 | 359.5 |
| Magnesium Carbonate | $MgCO_3$ | 111.5 | 1.3 |
| Calcium Carbonate | $CaCO_3$ | 175.2 | 6.3 |
| Iron Carbonate | $FeCO_3$ | 2.7 | .0 |
| Silica | $SiO_2$ | 20.5 | 21.0 |
| Alumina | $Al_2O_3$ | .9 | 2.2 |
| Total..... | | 383.6 | 433.4 |

These results are more accurate than those obtained by the other methods and hence show the actual amount of Ca and Mg left in the water after treatment with permutit.

## SOFTENING OF WATER CONTAINING SULFATES.

A run was made with a well water of the following composition:

(Results in parts per million)

| | | |
|---|---|---|
| Residue on evaporation | | 672. |
| Silica | $SiO_2$ | 11.4 |
| Chlorine | Cl | 40.0 |
| Sulfate | $SO_4$ | 133.8 |
| Potassium | K | 6.54 |
| Sodium | Na | 76.24 |
| Iron | Fe | .25 |
| Alumina | $Al_2O_3$ | 61.4 |
| Magnesium | Mg | 39.46 |
| Calcium | Ca | 83.65 |

Hypothetical Combinations

| | | |
|---|---|---|
| Potassium Chloride | KCl | 12.4 |
| Sodium Chloride | NaCl | 56.1 |

| | | |
|---|---|---|
| Sodium Sulfate | $Na_2SO_4$ | 166.8 |
| Magnesium Sulfate | $MgSO_4$ | 31.1 |
| Magnesium Carbonate | $MgCO_3$ | 114.9 |
| Calcium Carbonate | $CaCO_3$ | 208.6 |
| Silica | $SiO_2$ | 11.4 |
| Alumina | $Al_2O_3$ | 61.4 |
| Total..... | | 662.7 |

A very short run was made because of difficulty in obtaining the water.

Sample #1. Raw water.

Sample #2. Taken 2:15 p.m. Rate 32 gal. per hour.

Sample #3. " 2:30 " " 34 " " "

Sample #4. " 3:00 " " 33 " " "

The above samples were analyzed by the "rapid boiler" method.

| No. | Kind | N.C.H. | Alk. | Mg as $CaCO_3$ | $MgCO_3$ | $CaCO_3$ | $Na_2CO$ | Gal per Hour |
|---|---|---|---|---|---|---|---|---|
| 1 | Raw | +104 | 225 | 136 | 114.8 | 193 | ---- | ---- |
| 2 | Treated | -310 | 320 | 000 | 000 | 10 | 328.6 | 32 |
| 3 | " | -226 | 231 | 000 | 000 | 5 | 239.6 | 34 |
| 4 | " | -216 | 221 | 12 | 10.1 | 5 | 228.9 | 33 |

REMARKS.

The above results show that a water containing a large quantity of sulfates of calcium or magnesium can be softened by means of permutit as well as a water that contains only the bi-carbonates.

## COST OF SOFTENING WATER BY THE PERMUTIT METHOD.

All of the runs made with the permutit filter show that it will soften the University tap water, which has a hardness of about 300 parts per million of $CaCO_3$, at a rate of 33 gallons per hour for 15 hours before it is necessary to regenerate the filter.

It requires 8 pounds of salt for one regeneration. Thus 8 pounds of salt will soften, by using permutit, 15 times 33 or, approximately, 500 gallons of water.

Assuming the cost of salt at $3.50 per ton, which is rather high because salt of an inferior grade may be used, then we obtain $2000 \div 8$ or 250 regenerations for $3.50 or $250 \times 500 = 125{,}000$ gallons softened for $3.50. Hence it costs $350 \div 125$ or 2.8 cents per thousand gallons to soften the University of Illinois water to zero. Not enough experimental data is available to estimate the cost of softening the well water.

The following brief abstracts show the possibility of the practical use of sodium-permutit for softening water in a few industries.

Basch* in an article on "The Use of Permutit to Purify

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*Jour. Ind. & Eng. Chem. 4, 851.

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Feed Waters," states that the presence of alkali in waters prevents the corrosion of iron but causes foaming; and that the presence of NaCl counteracts the effect of the alkali. Hence waters treated with permutit cause foaming and yet do not prevent

corrosion because of the presence of small quantities of NaCl. However, other writers* state that at least 50 boiler plants in

*Practical Eng. June 1, 1912.

Germany, and over one thousand in Germany, France, England, and the United States are employing this system of treatment and none of them have had any trouble with corrosion, scale or foaming since this process was introduced.

It is claimed* that for dyeing and bleaching purposes,

*Textile World Record. Mar. 15, 1912. T. R. Duggan.

water treated by the permutit method is equal to distilled water. Hence it has great possibilities in the textile industries, because, aside from the saving of soap effected, the formation of the insoluble calcium and magnesium soaps in the fabrics is prevented, thus eliminating a constant source of trouble. The great success of the French silk industry is acknowledged to be due to the purity of the water used. Yet the largest French silk houses have installed the permutit process to remove the small degree of hardness of the water.

The use of permutit for laundry purposes has many advantages over the lime and soda processes. Water cannot be softened to less than 3.5 grains per gallon or 60 parts per million ($CaCO_3$) hardness by the lime and soda process* while it can be softened

*National Laundry Journal, May 15, 1912.

to zero by means of permutit. The cost of treatment is approximately the same with either method. The permutit treated waters

also contain a considerable quantity of bicarbonates which aid in cleansing and are ordinarily added to waters used for laundry purposes. Another important advantage of the permutit filter for laundries is that it automatically adjusts itself to waters of varying degrees of hardness. The mechanical adjustors used on the lime and soda softeners are efficient for a short time, although they require constant attention, but the action of the lime soon throws the gears out of adjustment and hence the water is not properly treated. All these difficulties are avoided in using a permutit softener.*

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*H. J. Wheaton, Nat'l Laundry Jour. Mar. 15, 1912.

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H. G. Anders* recently published the results of his

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*Wochenschrift für Brauerei, 28, 78.

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investigations of permutit for use in breweries. His results show that complete separation of calcium and magnesium from the water can be made without difficulty, and he states that waters treated by this method fulfill all the requirements of boiler feed waters. However, upon investigating this water for use as mash and soaking waters he found that small quantities of sodium carbonate were present, and this is very deleterious to the action of malt and hops in the sweetening, clarifying and improving the taste of beer. It was found that this sodium carbonate was formed through the action of the $CO_2$ in the water upon the permutit.

Mr. Anders concludes that water treated with permutit is unsuitable for mash or soaking water because the alkali carbonates of the permutit-treated waters are less desirable than

the calcium salts of the natural waters, because they are not precipitated out upon cooking. Also the sodium-bi-carbonate is broken down by high temperature to sodium carbonate which is very disadvantageous.

Thus it seems that permutit-treated waters can come into use in breweries only for boiler feed purposes.

In conclusion some of the advantages claimed for the use of permutit are:*

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*Chem. Rev. Felt-Harz Ind. 16, 300-2.

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1. Any water may be softened to any degree of hardness by regulating the flow.

2. The filter works automatically.

3. Variations in the feed water do not affect the filtrate.

4. The number of regenerations of the filter is unlimited.

5. Iron, manganese, organic matter, and bacteria may be removed by using manganese-permutit.

6. The process may be used in other industries; for example, to recover potassium from the waste of sugar refineries.

From my own investigations I have determined:

1. That calcium and magnesium can be completely removed from University tap water, and from a well water containing a large amount of sulfates.

2. That iron can be removed from the water by passing through the sodium permutit filter.

3. That the rate of flow may vary a great deal without affecting the quality of the filtrate.

4. That the filter can be completely regenerated.

5. That there is a small loss of permutit in washing the filter. However this loss is purely mechanical and by exercising a little care in flushing can be reduced to a minimum.

Although there has been, up to the present time, very little investigation of permutit, however, the results obtained both in this country and abroad all show the high efficiency and low cost of treatment of this method of water purification and point toward a large industrial application of the process in the future.

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